CHAPTER I
INTRODUCTION
Organic reagents have long been used as an effective tool in analytical chemistry for the simpler and cleaner separation, detection and determination of metal ions at macro and micro concentrations from mixture of coexisting components owing to their least solubility in water, selective colour reaction and complex formed with metal ions of definite composition and usually bright coloured. Hence, a numerous organic reagents e.g. oxine, oximes, triazines, cupferron, dithizone, hydroxamic acids, pyrocatechol, pyrogallol, gallic acid, alizarin, hydrazones, high molecular weight aliphatic amines, etc. (1-8) have been reported in search of a specific reagent for a particular metal ion. In continuation of these, new series of organic compounds "Amides and Amidines" have been recently introduced as extractants in presence of other complexing agents i.e. thio-cyanate, halides for the determination of the transition metals i.e. Ti, Nb, Mo, W, Re, Au, As, Sb, Bi, (9-20). They are basic in nature and usually form ion-pair complex or adduct with transition metal ions. They have certain advantages over commonly used organic reagents (1-8).
1. Extraction capacity of amidines is high.

2. Their colour reaction towards metal ions are highly selective.

3. They enhance the colour intensity of the binary complexes remarkably.

4. In the case of the some complexes e.g. Mo(V) -SCN, Sb(III)-I they stabilize the oxidation state of metal.

Of the various amides tested, only those derived by condensation of acetic anhydride with aliphatic or aromatic amines are found to be suitable extractants for the spectrophotometric determination of metal ions (12-13, 15).

The substitution of -OH group of amide by -SH (as in thioamide) greatly enhances the colour intensity of the Mo(V)- and W(V)- thiocyanate complexes (20). However, with amidines, the substitution effect is not well pronounced for the extraction spectrophotometric determination of the metals e.g. Mo(V), Ti(IV), Nb(V), W(V), Re(IV), Au(III), As(III), Sb(III), Bi(III) in the presence of other ligands may be due to high basic property (9-11, 14, 15, 16, 17-19).
Aliphatic amides, I, used were synthesized by condensation of acetic anhydride with aliphatic or aromatic amine as described in the literature (21) and the product obtained was crystallized from dilute ethanol (50% V/V), (21).

$$(\text{CH}_3\text{CO})_2\text{O} + \text{RNH}_2 \rightarrow \text{CH}_3\text{CONHR} + \text{CH}_3\text{COOH}$$

(I)

The thioamide, II, was prepared by sulphonation of the amide with $\text{P}_2\text{S}_5$ as in the literature and crystallized from dilute ethanol (22).

$$5 \text{CH}_3\text{CONHR} + \text{P}_2\text{S}_5 \rightarrow 3 \text{CH}_3\text{CSHNR} + \text{P}_2\text{O}_5$$

(II)

Amidines are amine derivatives of imidic acid, and in this investigation prepared by condensation of imidoyl chloride with amine. The imidoyl chloride, III, was prepared by chlorination of amide with thionyl chloride, (23), and the imidoyl chloride obtained was condensed with amine in equimolar ratio (24). The amidine hydrochloride, IV, so formed was treated with dilute ammonia to liberate the corresponding free base (V). The free base was recrystallized from dilute ethanol.
Ar-C = N-R + SOCl$_2$ --> Ar-C = N-R + SO$_2$ + HCl

OH
Cl

(III)

Ar - C = N.R + Ar.NH$_2$ --> Ar - C = N-R +

Cl
Ar - N - H

(III)

(IV)

Ar - C = N-R +

Cl
Ar - N - H

(IV)

(V)

Ar = Phenyl ring; R = Aryl or (CH$_2$)$_7$.CH$_3$

The purity of all these compounds was checked by m.p method. The solution of these compounds in various organic solvents was stable for at least one week when kept in coloured bottle. Amidines are slightly soluble in water whereas amides and thioamides are considerably soluble.
REVIEW OF EARLIER WORK

Previously amides and amidines have been used for extraction spectrophotometric determination of Ti(IV), Nb(V), Mo(V), W(V), As(III), Sb(III), and Bi(III) in presence of thiocyanate, bromide or iodide (9-12, 14, 17-19). They improve the selectivity of respective classical method with enhanced sensitivity. In addition, they also widen the working optimum acidity range.

SCOPE OF THE PRESENT INVESTIGATION

The review of earlier work show that they have wide scope for separation and determination of various other metal ions. In this investigation, ten amides, one thioamide and nine amidines were used for the extraction-spectrophotometric determination of Mo(V), W(V), Re(IV) and Au(III) in the presence of other ligands, e.g. SCN, Br.

Chapter II deals with extraction-spectrophotometric determination of Mo(V)-SCN complex with N-Phenylthioamide in benzene from hydrochloric acid solution. The method is selective and applicable for the determination of the metal in a variety of complex materials. The detailed studies of analytical variable on the extraction of the metal with these cited, ligands and composition of the complex are discussed.
Chapter III describes the extraction-spectrophotometric procedure for the determination of W(V) with thiocyanate and amides or N-phenylthioacetamide in benzene. The detailed studies have been made with the simplest compounds namely N-phenylthioacetamide and N-phenylacetamide. The reproducibility of the method has been tested to steel samples.

Chapter IV introduces an analytical procedure for the extraction-spectrophotometric determination of Re(IV) with thiocyanate and amides or thioamide. The basic compounds N-phenylacetamide and N-phenylthioacetamide were used for the detailed studies. The method has been applied for the recovery of the metal to low grade ore.

Chapter V describes a highly selective extraction-spectrophotometric method for the determination of Au(III) with bromide and N,N'-diarylbenzamidines in low grade ore. The detailed study with N-phenyl-N'-octylbenzamidine is made. Composition of the extracted complex and the effect of analytical variable on the extraction of the metal are discussed.
REFERENCES:


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